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Next Generation Flow Batteries

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Pacific Northwest National Laboratory

Support from DOE Office of Electricity Delivery & Energy Reliability Energy Storage Program

EESAT/Energy Storage Systems Program Review
Portland, OR
September 23rd, 2015

Introduction of Redox Flow Battery(RFB) Technology

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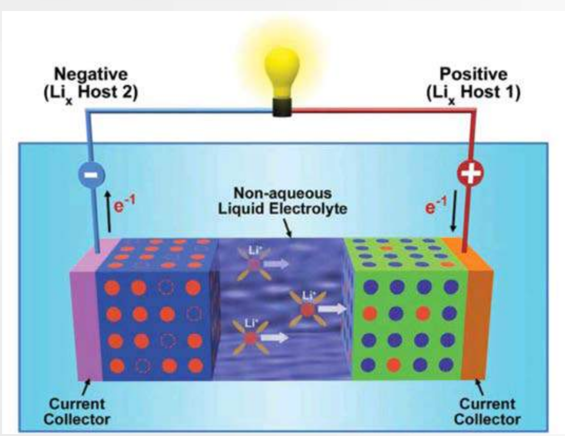
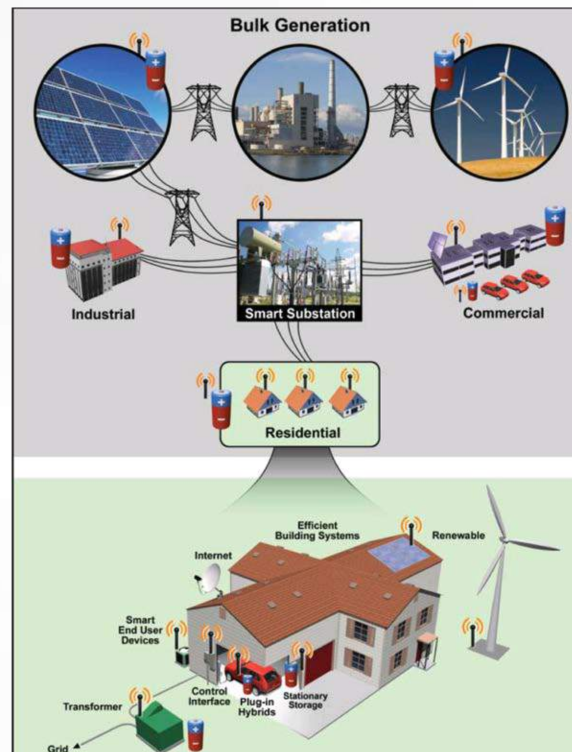
Applications

- Renewable energy integration
- Improve grid reliability
- Enable smart grid deployment
- Support electrification of the transportation sector





Project Overview

Energy Storage Challenge

- Development of cost and performance competitive RFBs for stationary energy storage application.

Project Objective

- Identify and develop future RFB systems with potential to reach cost target.

Accomplishments

- Identified and demonstrated a new redox chemistry
- Investigate the Nafion membrane morphology and its impact on VRB performance.
- Developed an organic nonaqueous RFB system and investigated its capacity decay mechanism.
- Development of high-performance catalytic electrode for Zn-I RFB.
- 10 publications, 2 patents applications, 3 patents granted in 2015 (to date)

PNNL Roadmap for Redox Flow Battery Development

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Cost $/kwh: 600, 500, 400, 300, 200, 100

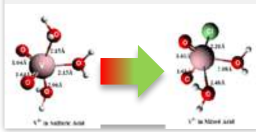
Current density mA/cm²: 100, 200, 300, 400

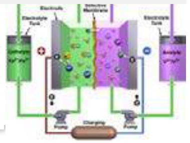
Performance

Cost

Gen I Redox Chemistry

Mixed-acid VRB | Fe-V RFB

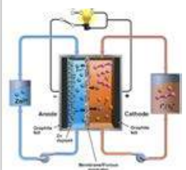


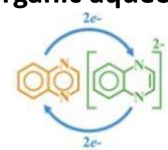


Tradition flow field

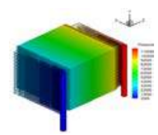
Gen II Redox Chemistry

Zn-I RFB | Organic aqueous





InterDigital flow



Gen III System

- Novel electrolyte
- Catalytic electrode
- High conductive membrane
- High power stack

2010 — 2015 — 2020

Fuel utilization>60% EE>70%

A Total Organic Aqueous Redox Flow Battery

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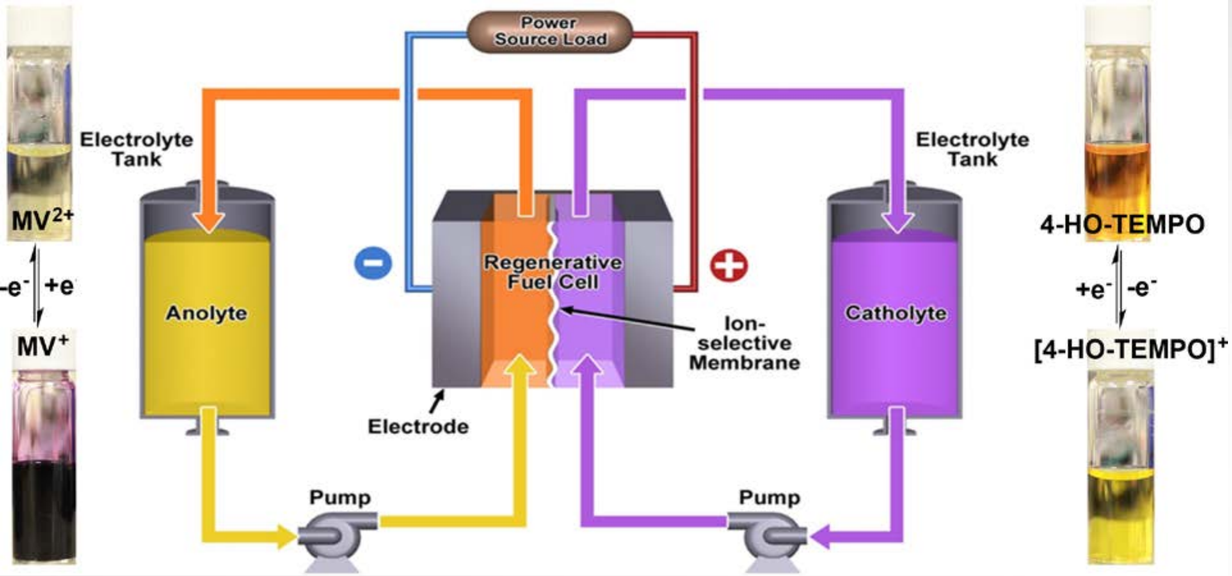
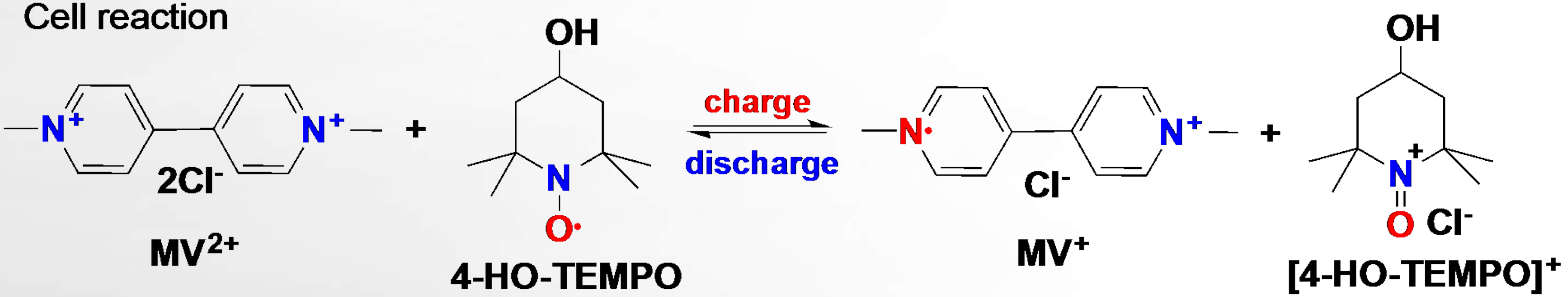


Advantage:

- Low-cost redox couple;
- Low-cost supporting electrolyte;
- No resource constraints;
- Less corrosive and toxic.

Cell reaction



Voltage of Aqueous Redox Flow Battery

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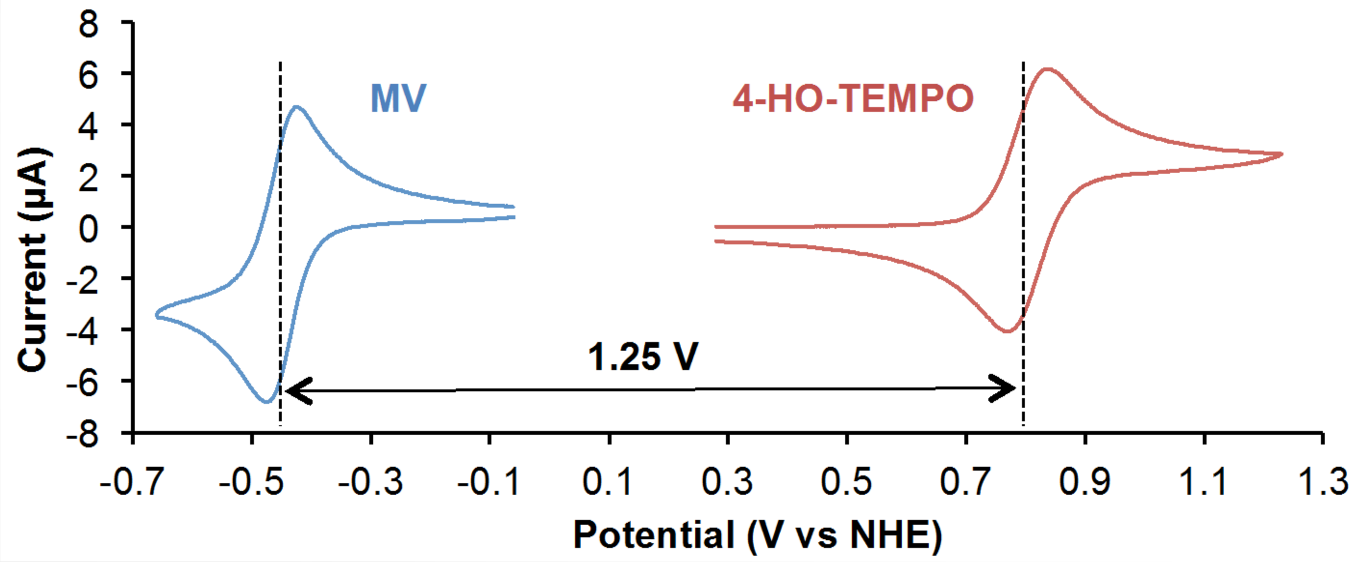
ARFBs (anolyte/catholyte)	Cell voltage (V)	Current density (mA/cm^2)	Supporting electrolytes	Membrane
$PbSO_4$/BQDS	1.07	10	H_2SO_4	Nafion 115
AQDS/Br_2	0.96	500	H_2SO_4 and HBr	Nafion 117
AQDS/BQDS	0.76	8	H_2SO_4	Nafion 112
MV/4-HO-TEMPO	1.25	60	NaCl	AME



Solubility in water:
MV > 3.0M
4-HO-TEMPO: >2.1M

Excellent Kinetics

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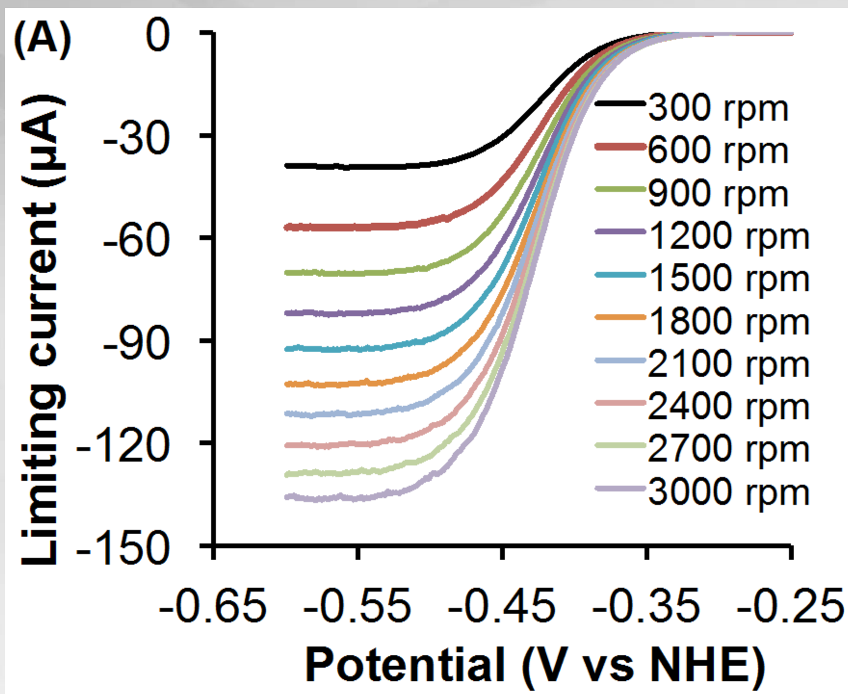
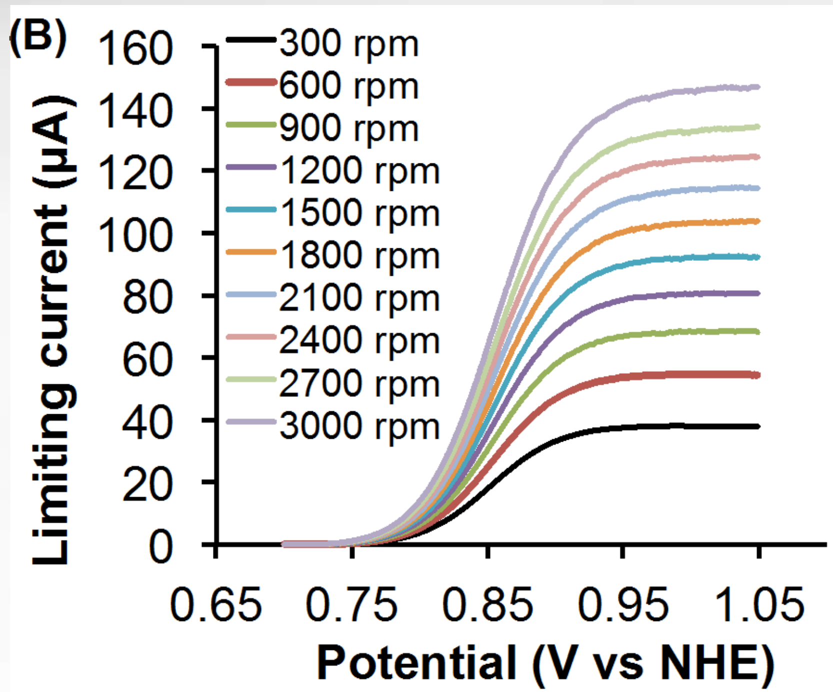


Linear sweep voltammograms of **MV**



Linear sweep voltammograms of **4-OH-TEMPO**

Excellent Kinetics

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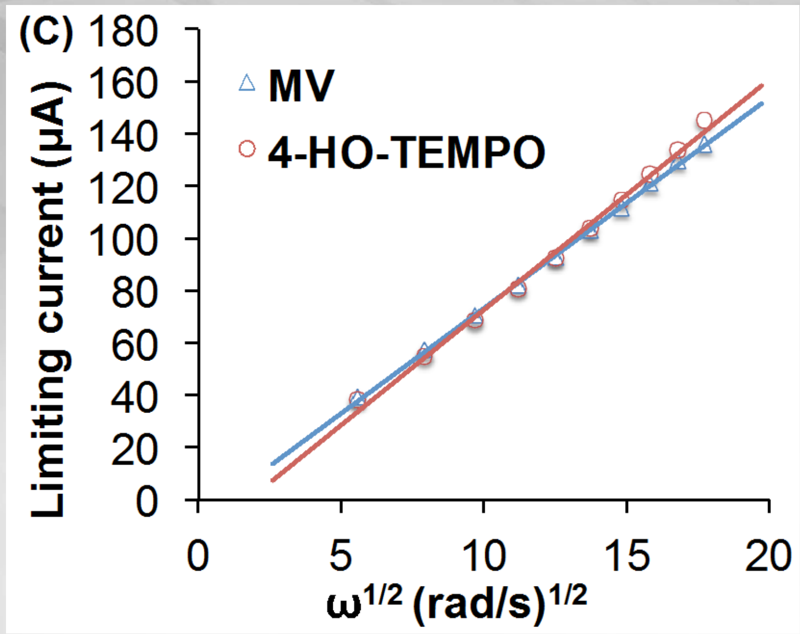
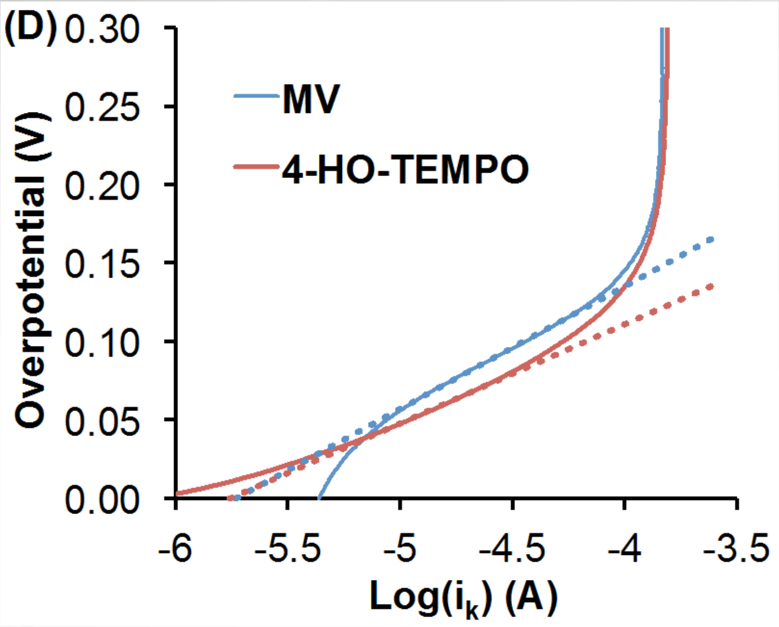


Levich plots of the limiting current vs the square root of rotation rates for **MV**(blue) and **4-OH-TEMPO** (red)

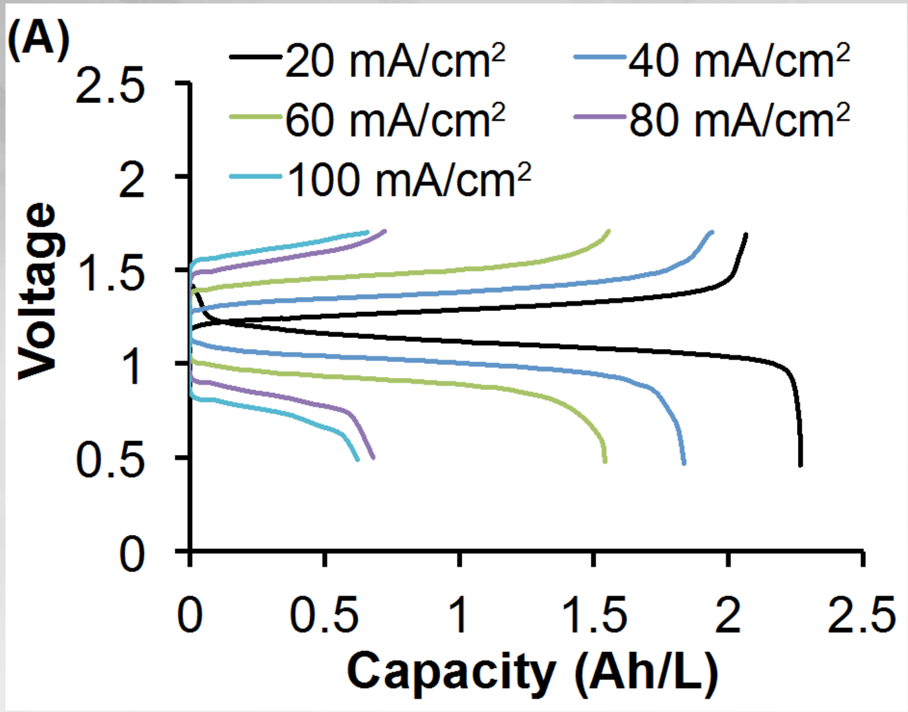


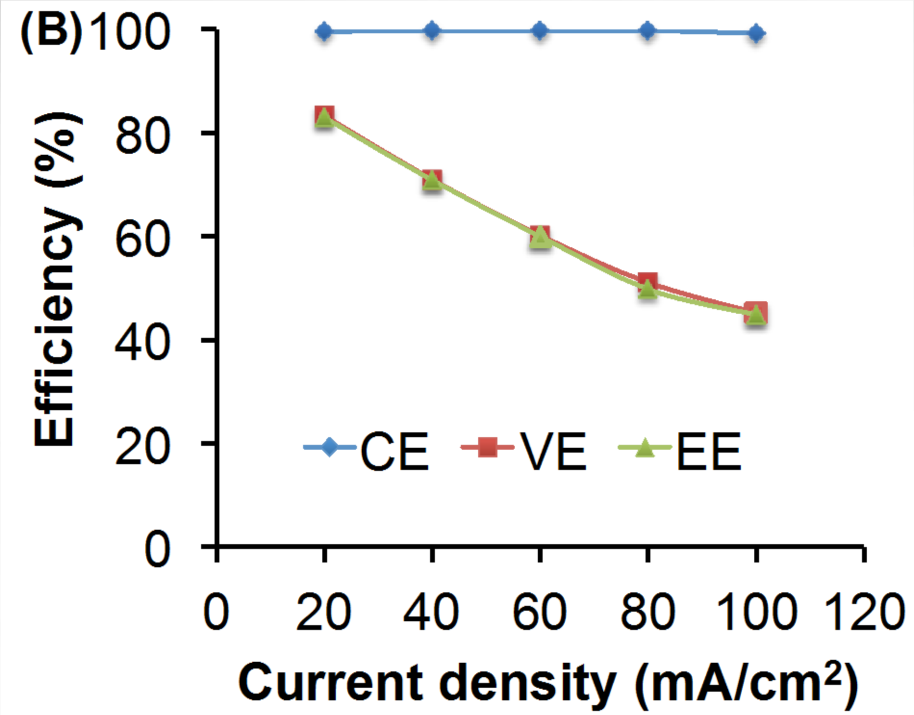
The plots of kinetic current versus overpotential and the corresponding fitted Tafel plots for **MV** (blue) and **4-OH-TEMPO** (red).

Redox couples	D ($\times10^{-6}$ cm^2 s^{-1})	k ($\times10^{-4}$ cm s^{-1})
MV	25.7	2.8
4-HO-TEMPO	29.5	2.6
$V^{4+/5+}$	5.7	0.02
AQDS/$AQDSH_2$	3.8	72

B. Huskinson, etc. *Nature* 505, 195, 2014.
Weber, etc. *J. Appl. Electrochem.* 2011, 41, 1137.

Flow Cell Performance – Low Concentration

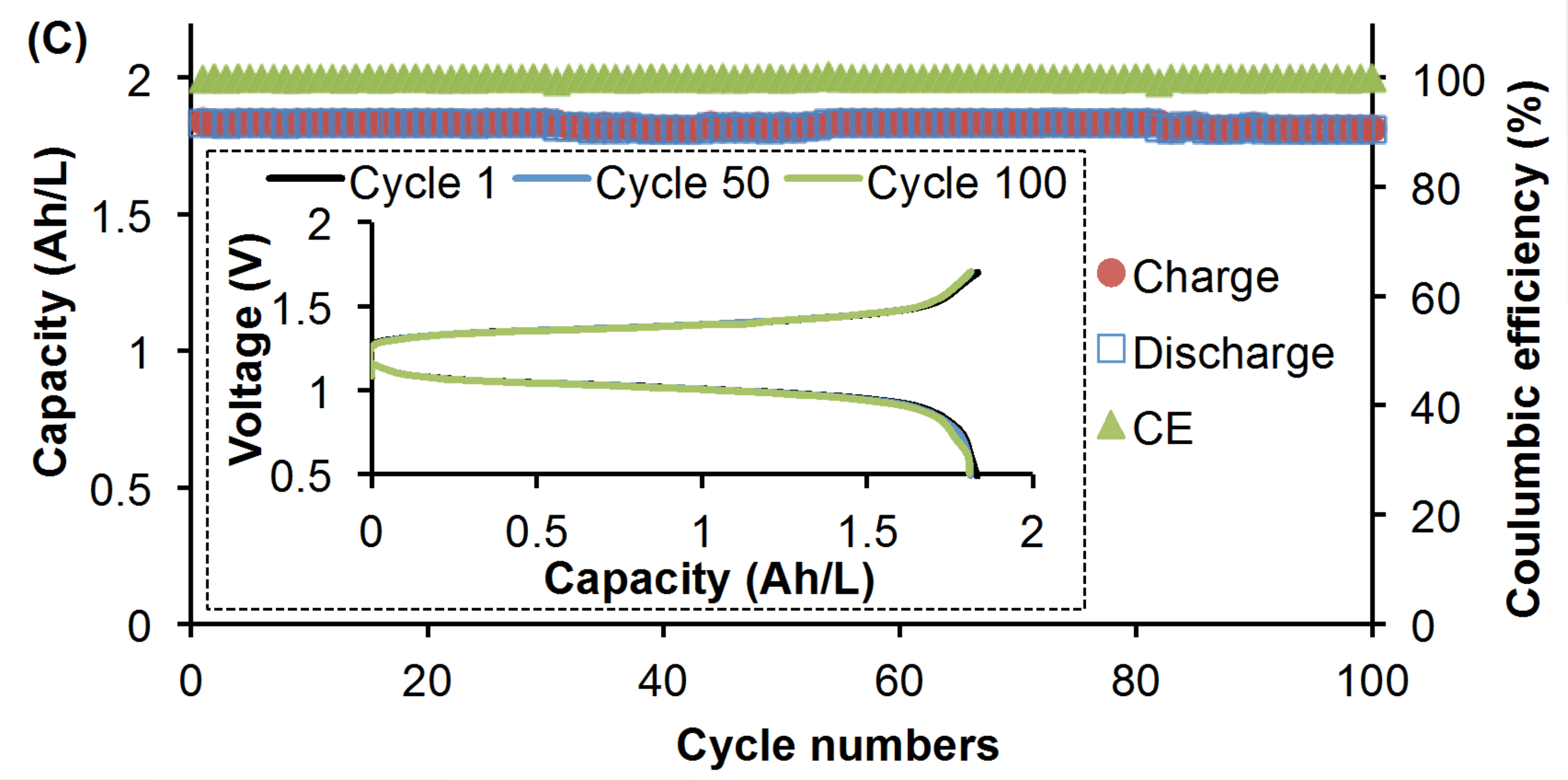




Representative charge and discharge profiles of the **MV /4-HO-TEMPO** ARFB (0.1M) at the cycling rates from 20 to 100 mA/cm^2.

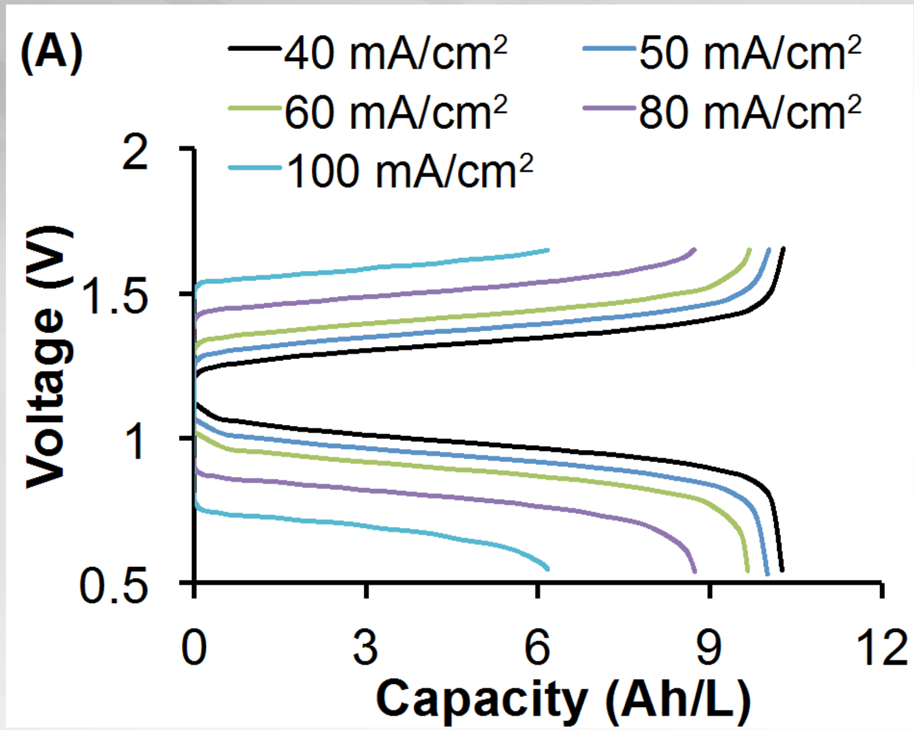
Plots of coulombic efficiency, voltage efficiency, and energy efficiency versus current density of the cell.

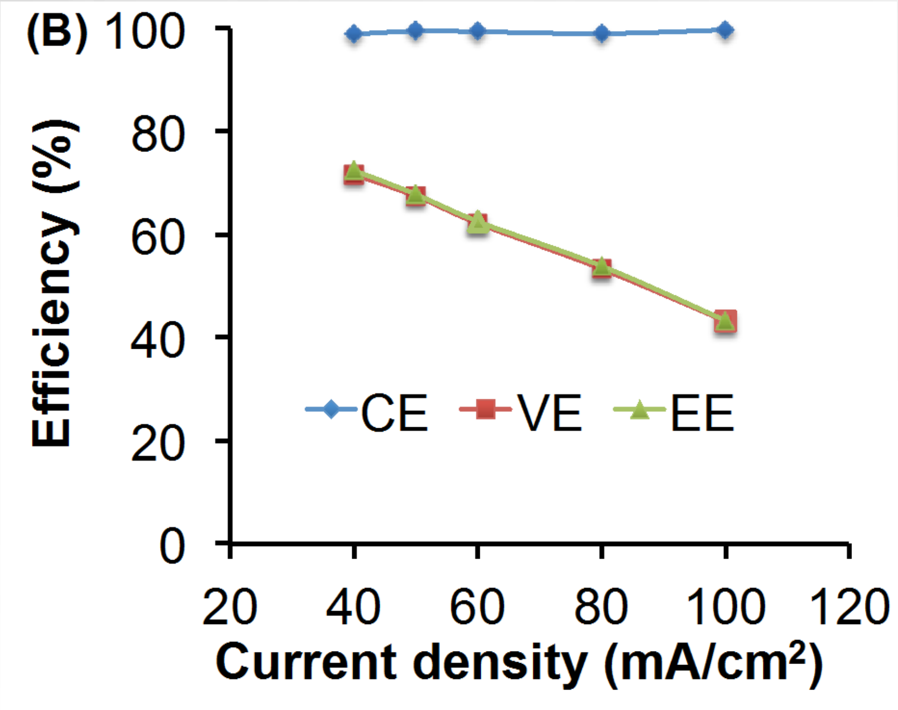
Flow Cell Performance – Low Concentration



Capacity and coulombic efficiency vs cycling numbers of the cell at 40 mA/cm^2. Conditions: anolyte, 0.1 M **MV** in 1.0 M NaCl aqueous solution; catholyte, 0.1 M **4-HO-TEMPO** in 1.0 M NaCl aqueous solution; flow rate, 20 mL/min; AMV anion membrane. No remixing.

Flow Cell Performance – High Concentration

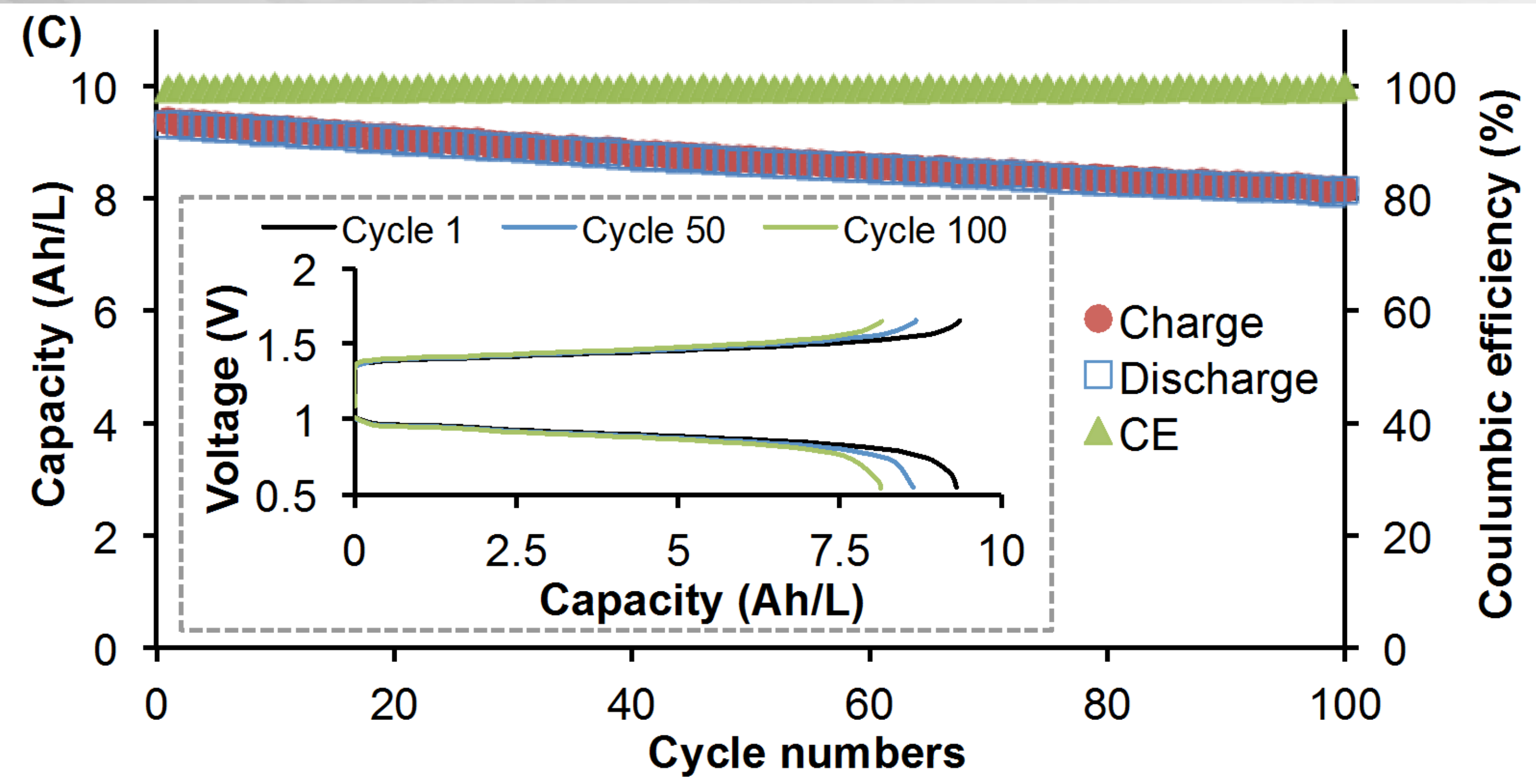




Representative charge and discharge profiles of the **MV /4-HO-TEMPO** ARFB (0.5 M) at the cycling rates from 20 to 100 mA/cm^2.

Plots of coulombic efficiency, voltage efficiency, and energy efficiency versus current density of the cell.

Flow Cell Performance – High Concentration



Capacity and coulombic efficiency vs cycling numbers of the cell at 40 mA/cm^2. Conditions: anolyte, 0.5 M **MV** in 1.5 M NaCl aqueous solution; catholyte, 0.5 M **4-HO-TEMPO** in 1.5 M NaCl aqueous solution; flow rate, 20 mL/min; AMV anion membrane. No remixing.

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Summary of the organic aqueous RFB

- A new MV and 4-HO-TEMPO based organic aqueous RFB is demonstrated with stable cycling performance at the current density of 40mA/cm^2 with theoretical voltage of ~1.25V;
- Preliminary cost analysis indicated a significant cost reduction compared with VRBs, mainly due to the low-cost redox active materials.

Other developments in the field of RFB

- Nafion membrane microstructure investigation;
- Nonaqueous RFBs development;
- High-performance catalytic electrode.

Please check out our electrode and nonaqueous RFBs research at poster session.

Correlating Nafion Membrane Microstructure with VRB Performance

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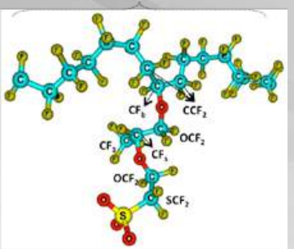
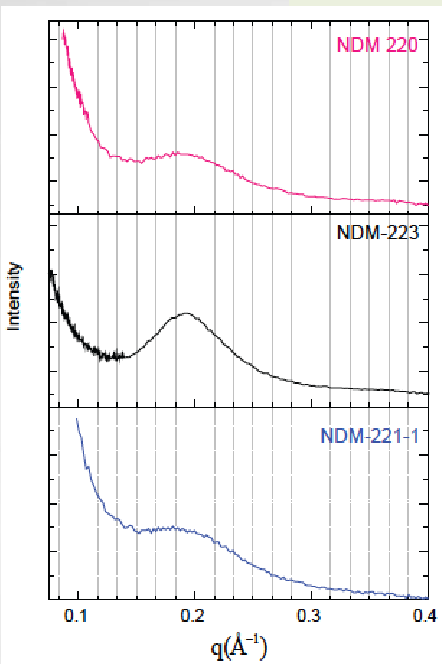
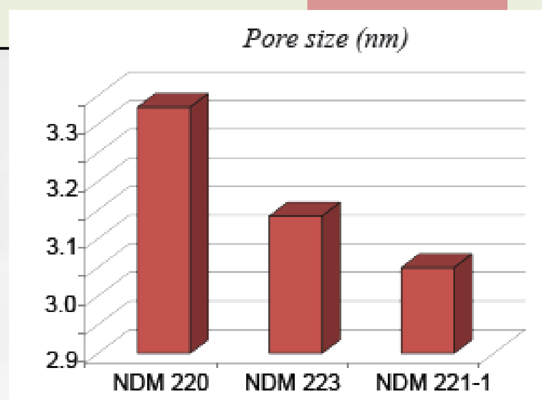
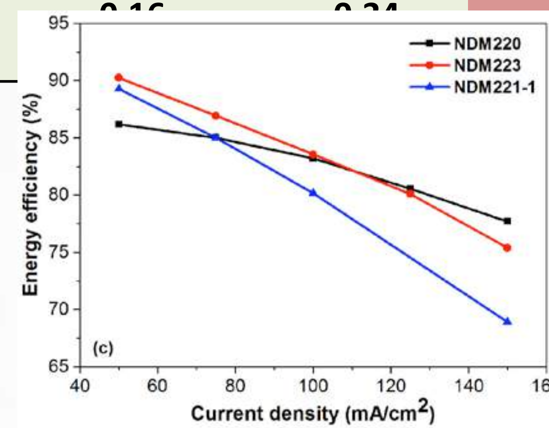
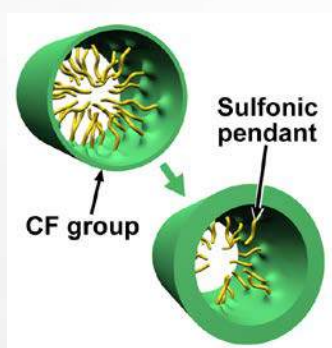


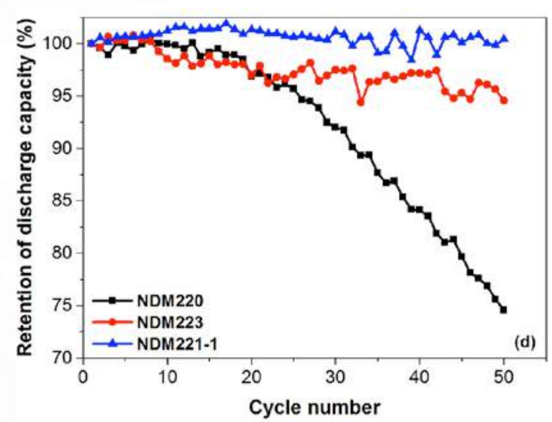
Membrane	EW	Thickness (µm)	Conductivity (mS cm^{-1})	Area resistance (mΩ cm^2)	Diffusion Coefficient of VO^{2+} (*10^{-6} cm^2 min^{-1})	VO^{2+} ion flux (*10^{-7} mol cm^{-2} min^{-1})	Selectivity Between H^+ and VO^{2+}
NDM220	1000	52	70.6	77.2	1.20	2.31	58.8
NDM223	1200	53	44.8	102.4	0.46	0.87	97.4
NDM221-1	150	47	18.8	222.8	[illegible]	[illegible]	116.8











Chemours™

Total Organic Nonaqueous RFB

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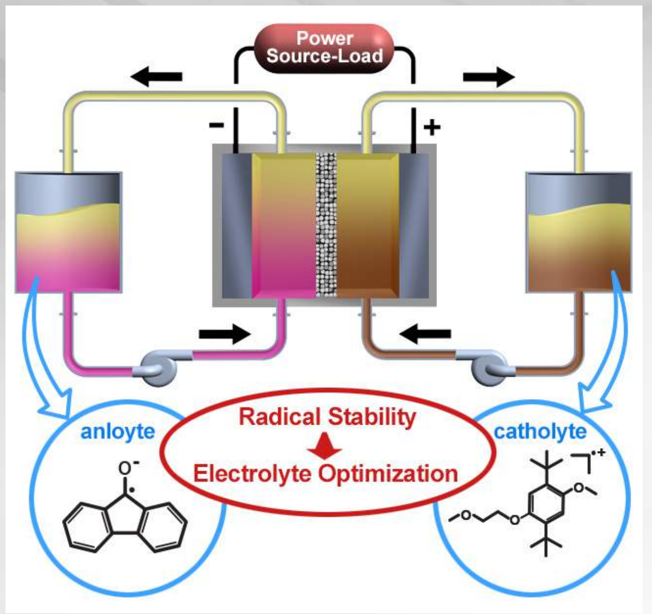

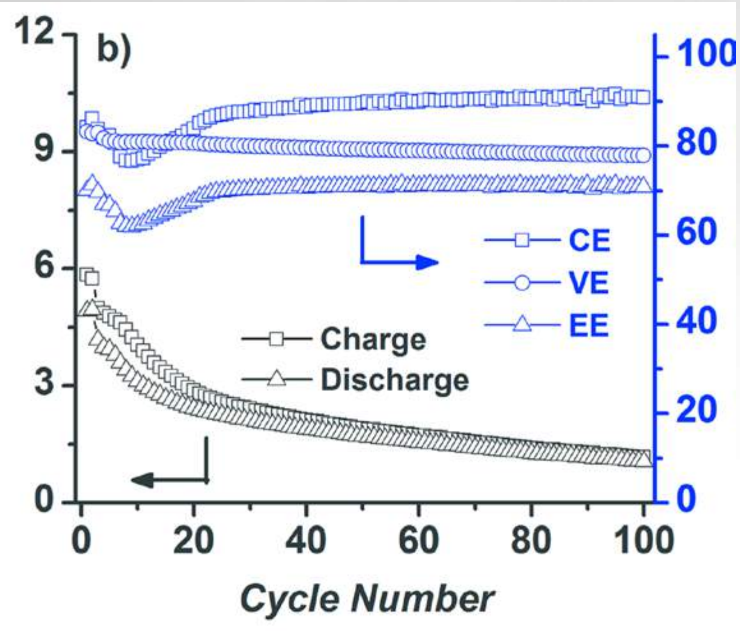

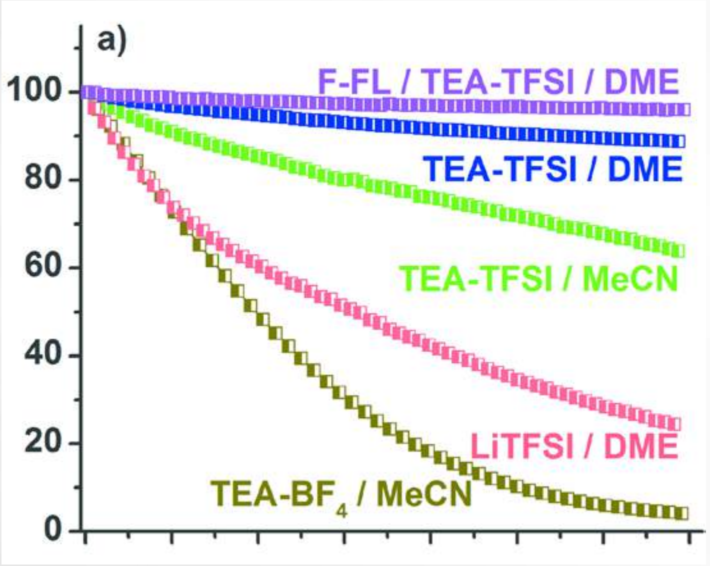

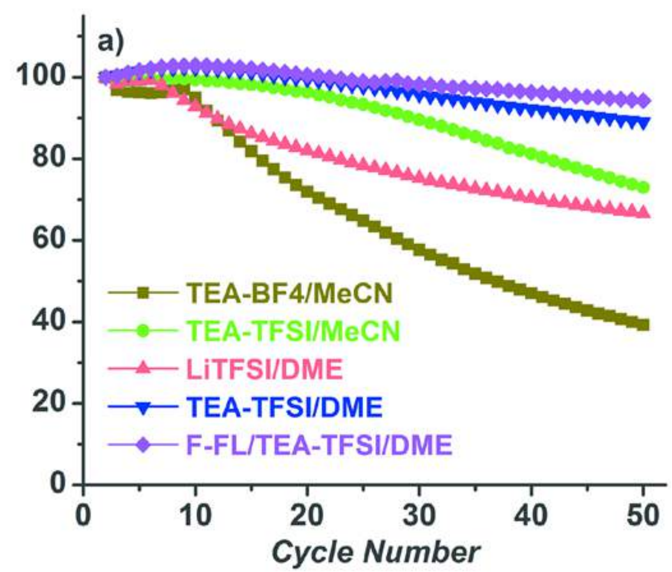

Conclusions

- A total organic aqueous redox flow battery system has been designed and demonstrated, which has great potential to be developed as next-generation low-cost redox flow battery system for stationary energy storage.
- Nafion membrane morphology and its impact on VRB performance were investigate.
- A nonaqueous RFB chemistry was developed, and its capacity decay mechanism was researched.

Future work

- Continuous optimization of the MV-TEMPO system.
  - Improving the current density through electrolyte optimization;
  - Identify and develop low resistance membrane;
  - Investigate and mitigate the capacity decay mechanism.

Acknowledgements

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- External collaborators
  - Sandia National Laboratory
  - Chemours (Formerly Dupont)